INVESTIGATION OF THE POLARIZATION BEHAVIOR OF URANIUM IN LiCl-KCl MOLTEN SALT

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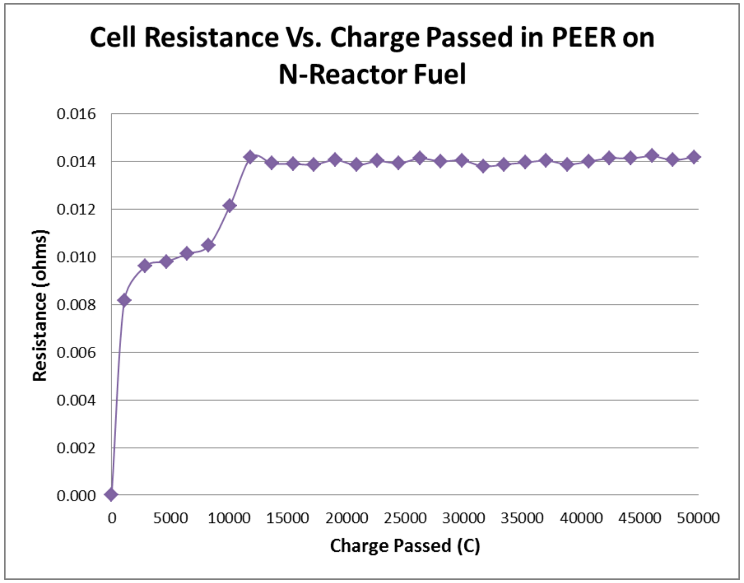
Electrorefining Experience

- Developing a corrosion theory based electrorefiner model
  - Requires detailed polarization behavior for uranium
  - Requires Tafel constant and exchange current density for U/U^{3+}
- Experiments conducted at engineering-scale with uranium to validate a process model
  - Observed flaking black salt film and residue in anode basket
  - Observed two step resistance behavior

Salt Film Observed on U



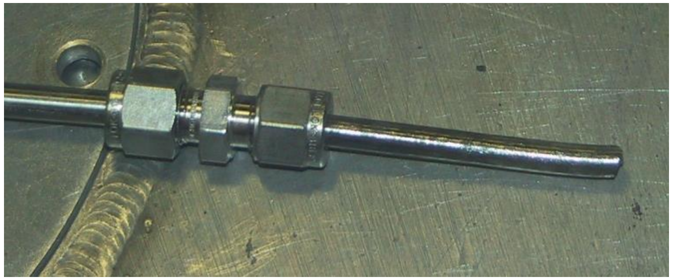
Goal

- Examine polarization behavior of uranium
  - Collect potentiodynamic data over wide potential range
  - Sample film material and analyze for composition
  - Develop mathematical model for polarization behavior
- Determine Tafel constant and exchange current density
  - Collect data in pre-Tafel Region to avoid film formation
  - Use Oldham-Mansfeld method to determine, β and i_o
- Use the polarization model and Tafel parameters to simulate electrorefining

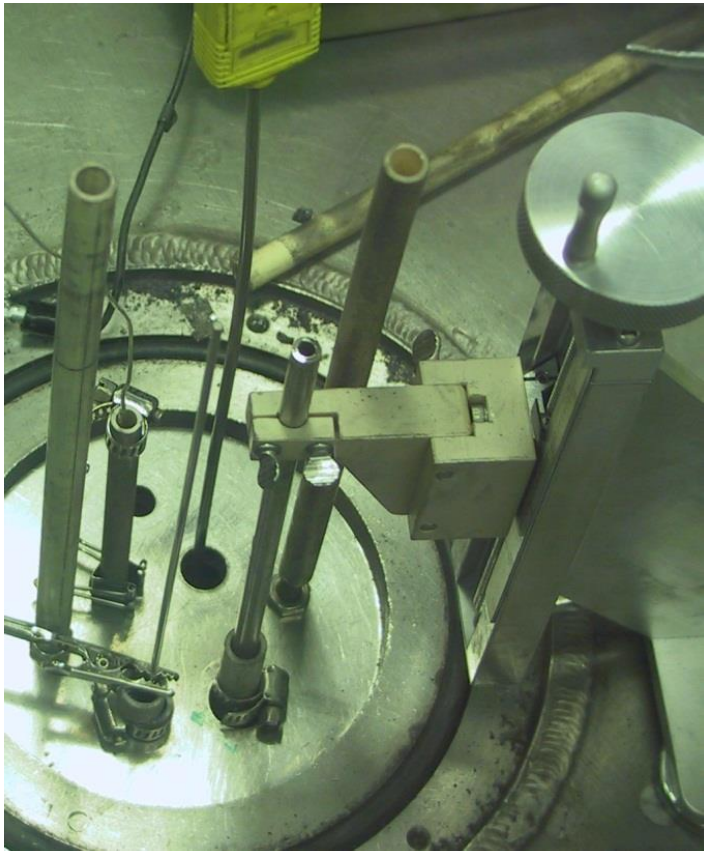
Experiment Design

- Studied anodic dissolution of U in LiCl/KCl eutectic
- Three Electrode Cell:
  - Working -Uranium rod
  - Counter - Tungsten rod
  - Reference –Ag/AgCl in Mulite
  - Solartron 1285 Potentiostat
- Potentiodynamic scans(PDS)
  - Temperatures range 450-650°C in 50° intervals
  - Scan rates of 0.1, 0.166 and 1mV/s
  - Scanned from -0.2V to0.5V
- Working electrode was raised/lowered using a vertical translator to give accurate control of immersion depth

Uranium Electrode



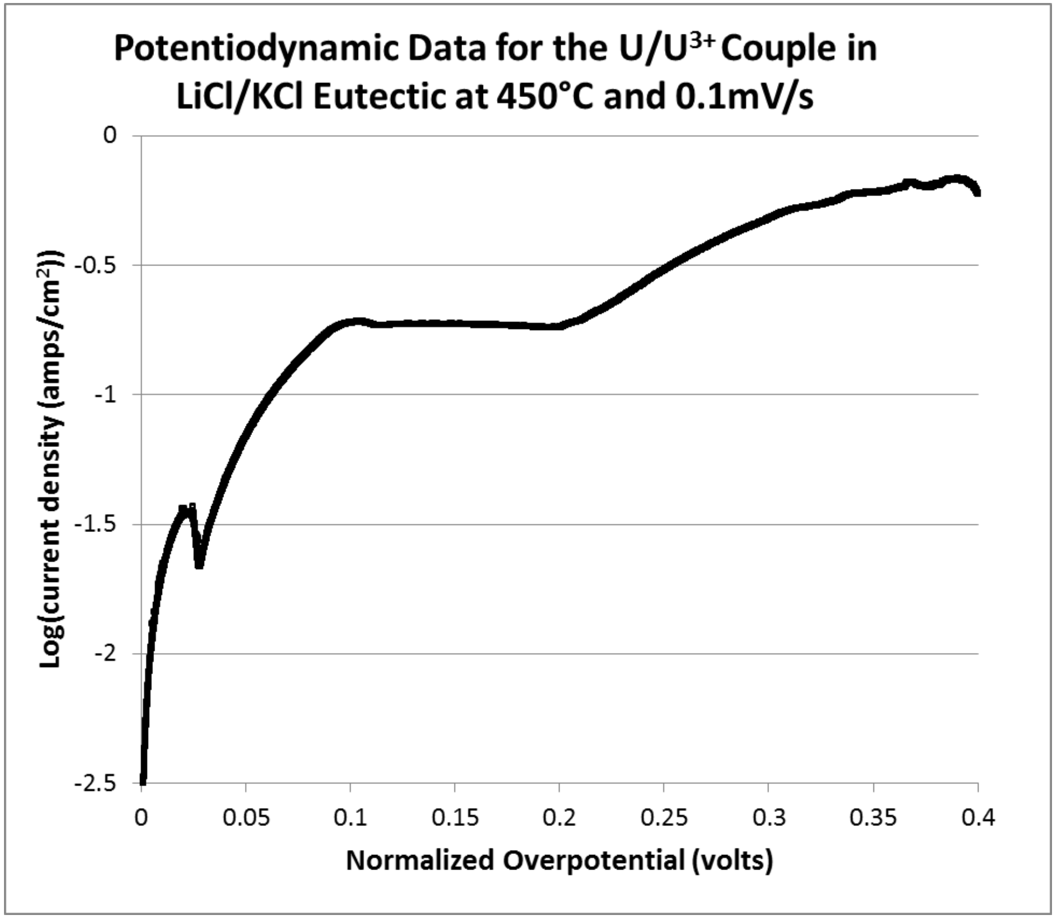
Electrodes and Vertical Translator Device of Test Cell



Low Temperature Anodic Behavior

Anodic PDS at 450 and 500°C showed several distinct features:

- Small reaction peak at low overpotential (10-50mV)
- Passivation at intermediate overpotential (125-275mV)
- Polishing dissolution at overpotentials above 250mV



Sample of anodic potentiodynamic data at 450°C and 0.1mV/s.

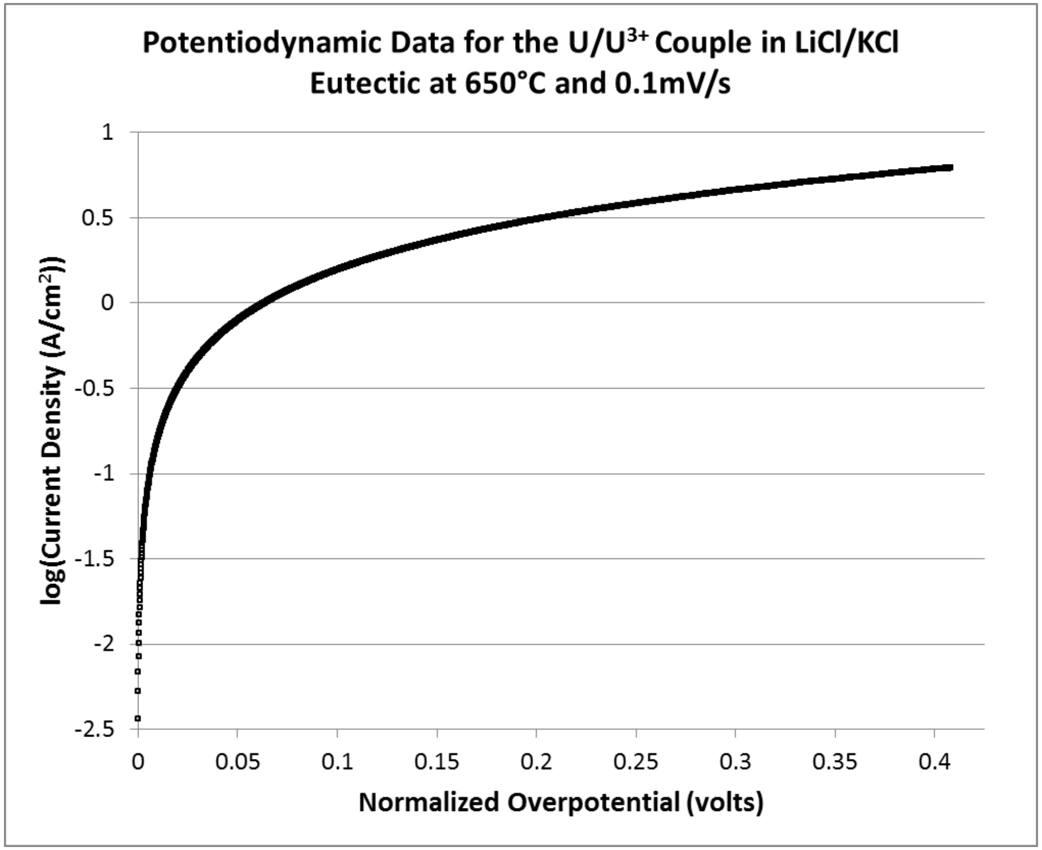
High Temperature Anodic Behavior

Anodic PDS at 650°C:

- Polarization follows Tafel behavior

Overall polarization behavior:

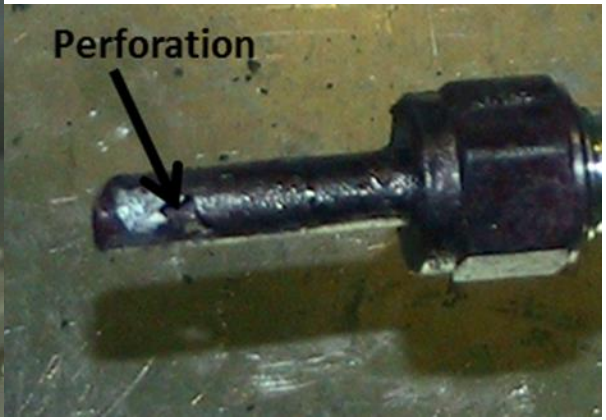
- Temperature dependent
- As T rises polarization features disappear



Sample of anodic potentiodynamic data at 650°C and 1mV/s

Film Analysis

- Film was removed from cooled uranium rod post-testing
  - Abraded with steel file, collected powder
  - Examined with XRD, SEM and ICP-MS
- Electrode was mounted in acrylic, and sectioned
  - Examined with SEM



- After PDS at 500°C, 0.01mV/s electrode was discovered to be hollow
- Powder removed from light gray section
  - Perforated electrode in the process

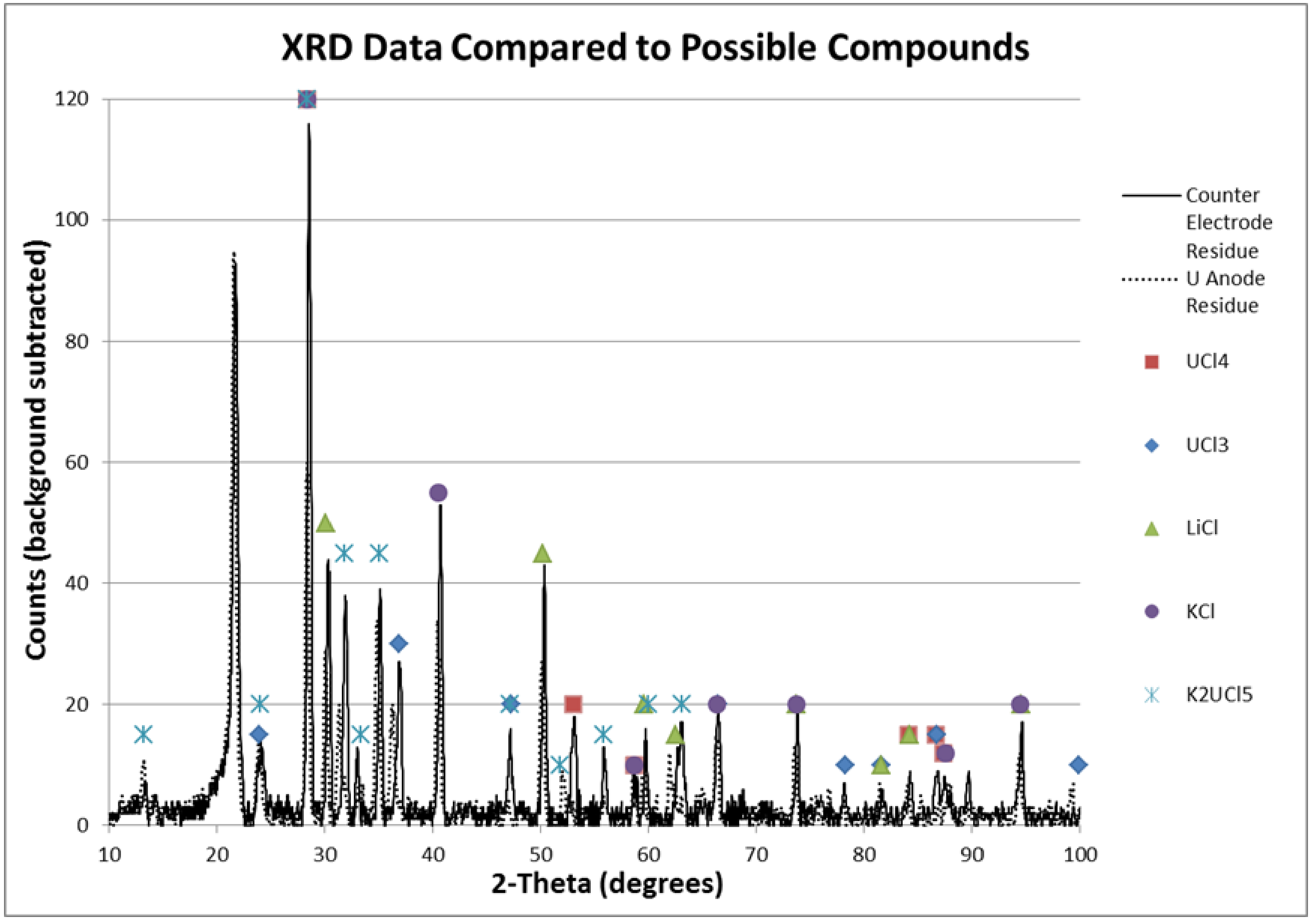
X-Ray Diffraction Data

Two powder samples analyzed:

- From uranium working electrode used in PDS experiments
- From preliminary experiment- uranium counter electrode

Film powder samples are a mixture:

- Electrorefiner salt (LiCl, KCl, UCl_3)
- K_2UCl_5



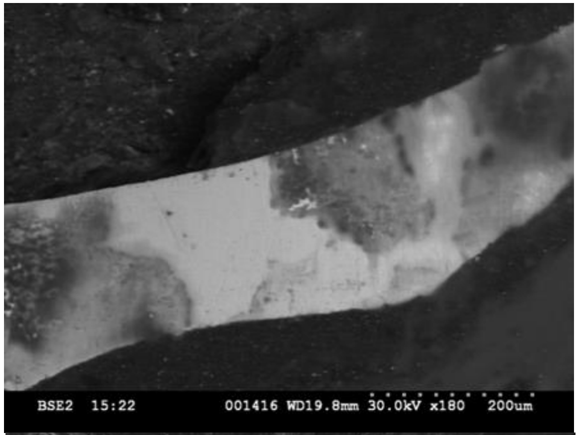
SEM and ICP-MS Data

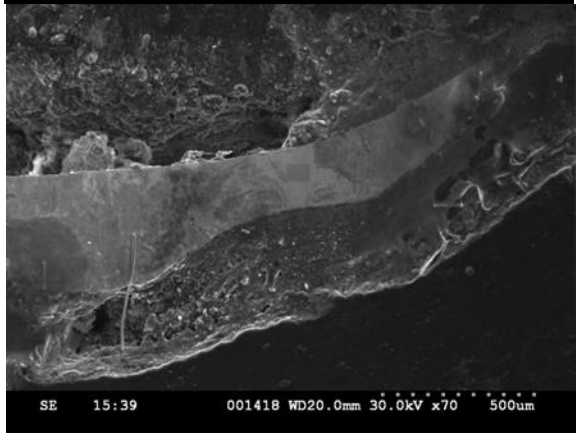
ICP-MS data for powder samples:

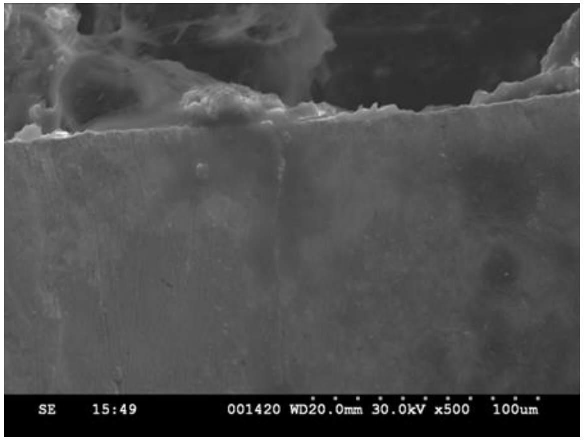
- Uranium working electrode
  - 2.77 mol % uranium
  - 96.6 mol% salt
- Uranium counter electrode
  - 0.24 mol% uranium
  - 79.7 mol% salt

SEM data for sectioned hollow rod:

- Used 30kV for analysis
- Showed non-uniform corrosion
- Evidence of cracks with enhanced corrosion at the surface
- Electrode-electrolyte interfacial uranium concentrations
  - 1.6 to 28.6 mol%







Explanation of Polarization Behavior

K_2UCl_5 precipitates at the electrode-electrolyte interface above a critical concentration

- Perhaps ~6 mol% at 450°C

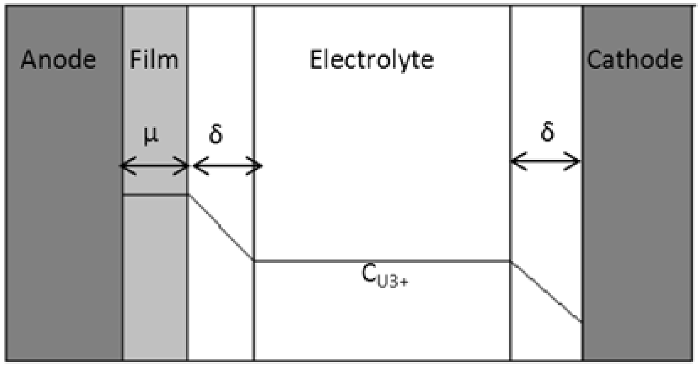
First feature in the low T polarization data is the onset of the precipitation

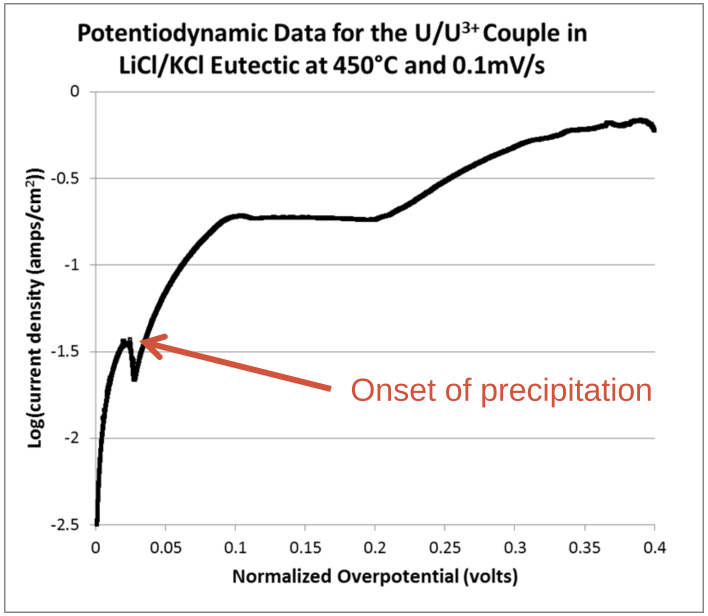
Passivation occurs when surface blockage is balanced with the polarization of the electrode

Breakdown of film occurs at > 250mV with two possible mechanisms

- Dissolution of film exceeds buildup
- Film develops internal stress and cracks

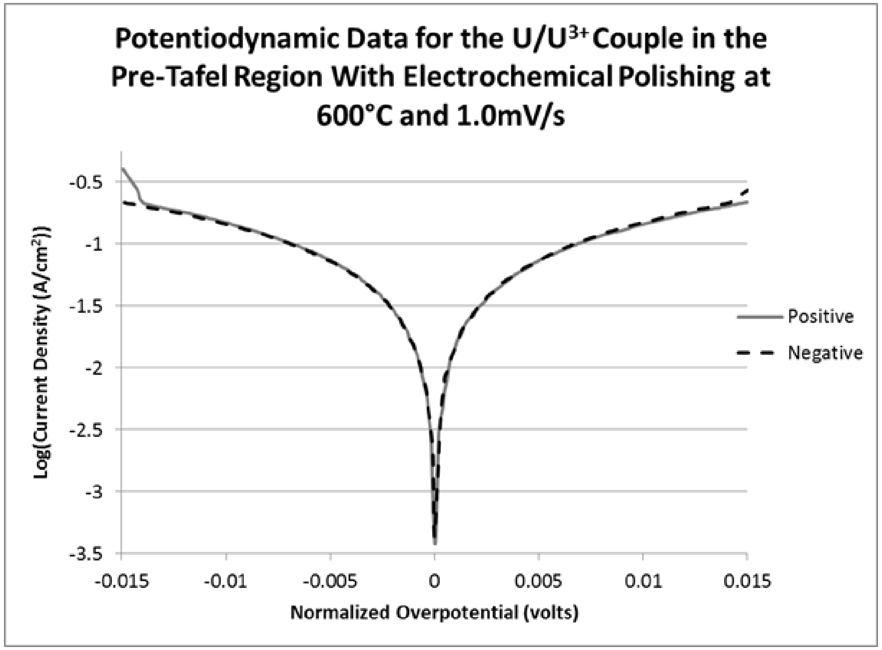
At T>626°C no solid phases are present in the LiCl-KCl-UCl_3 system





Tafel Constant and Exchange Current Density

- Scanned potentiodynamically in the pre-Tafel range, ±15mV, to avoid film formation
  - Electropolished at 7.5mV for 300s to create identical electrode surface
  - Allowed to equilibrate between tests after polishing
  - Positive and negative scan directions
  - Scan rates of 0.1, 0.166 and 1.0 mV/s
  - Temperatures between 450°C and 650°C in 50° intervals



Tafel Constants

Oldham-Mansfeld Method

−Find R_p at ± 1 mV from:

$$\left.\frac{d\eta}{di}\right|_{\eta_{corr}} = R_p$$

−Plot $2.3R_pi$ vs. η

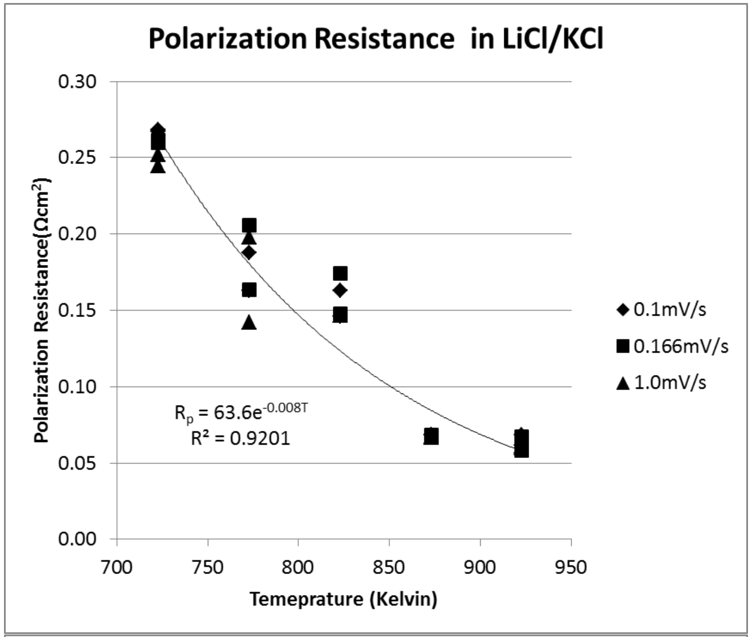
−Use Origin software to fit curve

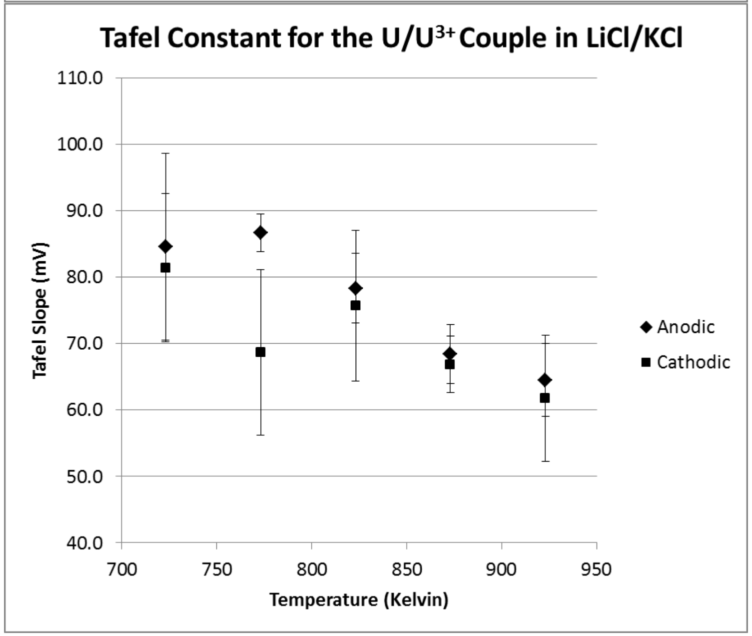
−Obtain β_a and β_c from:

$$2.3R_pi = \left[\frac{\beta_a\beta_c}{(\beta_a+\beta_c)}\right]\left(e^{\frac{2.3\eta}{\beta_a}} - e^{\frac{-2.3\eta}{\beta_c}}\right)$$

−Tafel constants show inverse relationship with T. Likely due to transfer coefficient's relationship with T

$$\beta = \frac{RT}{2.3\alpha(T)nF}$$





Exchange Current Density

Used Tafel constants fitted from Origin to find corrosion current density from :

$$i_{corr} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a + \beta_c)}$$

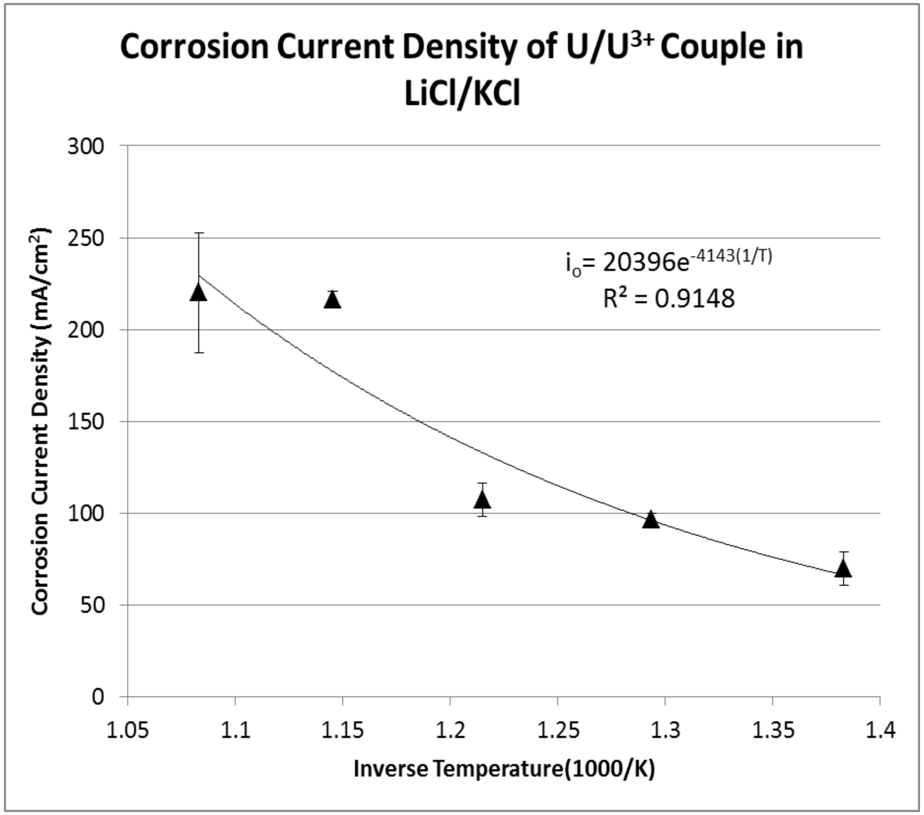
$i_{corr} = i_o$ (exchange current density) if only one redox couple is present

- Confirmed U/U^{3+} by CV

Calculated activation energy from Arhenius relationship

$$i_0 = nFAe^{\frac{-E_A}{RT}} [C_o]^{(1-\alpha)} [C_R]^{\alpha}$$

E_A =34.4kJ/mol



Comparison of Tafel Parameters to Literature

- Tafel slope at 500°C
  - reported by Gosh et al.- 98.5± 4mV
  - Reported here- 86.6± 2.8mV

- Exchange Current Density at 500°C
  - Reported by Gosh et al.- 8± 2mA/cm^2
  - Reported here- 96.6± 3.0mA/cm^2

- Differences in Method:
  - Gosh ignored the effects of low temperature uranium polarization observed in this work
  - Gosh used Tafel extrapolation of the anodic branch only
    - Not recommended by Scully

Summary

- Anodic PDS show temperature dependent behavior
  - At T<626°C
    - K_2UCl_5 precipitates as U^{3+} ions reach critical concentration in the diffusion layer
      - Presence confirmed by XRD
      - Likely forms at cracks and crevices
    - Kinetic balance between surface coverage and polarization causes passivation region of polarization curve
    - Breakdown occurs at η >250mV
  - At T>626°C
    - Simple Tafel behavior
- Pre-Tafel region PDS data gave precise β and i_0 by the Oldham-Mansfeld method
  - At 500°C: $\beta_a = 86.6 \pm 2.8$mV and $i_o = 96.6 \pm 3.0$mA/cm^2

References

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